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A TOOL FOR INFRARED STUDIES OF
WEAK CHARGE TRANSFER COMPLEXES

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This review gives a summary and discussion of the results from the following papers which will be referred to by the Roman numerals I-VI.

- I. Fredin, L., Rosengren, Kj. and Sunner, S.
A Variable Temperature Liquid Helium Cryostat for UV- and IR-spectroscopy.
Chemica Scripta 4 (1973) 93.
- II. Fredin, L.
A Constant Flow Double Nozzle for Matrix Isolation Spectroscopy.
Chemica Scripta (accepted for publication)
- III. Fredin, L.
An Exploratory Study of Weak Molecular Complexes in Low Temperature Matrices.
Chemica Scripta 4 (1973) 97.
- IV. Fredin, L. and Nelander, B.
On the Structure of the Ethylene-Chlorine Complex.
J. Mol. Struct. 16 (1973) 205.
- V. Fredin, L. and Nelander, B.
An Infrared and CNDO Study of a Water-Chlorine Complex.
J. Mol. Struct. 16 (1973) 217.
- VI. Fredin, L. and Nelander, B.
On the Structure of Benzene Halogen Complexes.
Mol. Phys. (accepted for publication)



INTRODUCTION

The term charge transfer complexes was introduced by Mulliken (1,2) who presented the now generally accepted theoretical description of these compounds (2). These complexes have been extensively studied (3,4,5) and one of the reasons for this is their possible function as intermediates in chemical reactions (6,7). Much work has been devoted to exploration of the structure of such complexes both by infrared spectroscopy (8) and x-ray crystallography (9). For the strong charge transfer complexes this is a relatively straightforward task. The strong complexes can be obtained in sufficient concentrations to make infrared studies quite workable and they usually form well defined entities within the unit cell of crystals. The weak complexes are much more difficult to study. The concentrations that can be obtained in solutions at room temperature are low (typically less than 5 %), and with the small changes in infrared spectra between the complex and the free components often encountered, the overlap between absorptions makes the measuring situation difficult. Furthermore crystals of these weak complexes are often built up by infinite chains and it is a matter of debate if the structures of these $n:n$ complexes in crystals have any bearing on 1:1 complexes in solution or the gas phase (3).

The spectral information that is obtained from infrared studies of weak charge transfer complexes is mainly of four kinds. Because of lowering of symmetry, transitions that are forbidden in the free components may be allowed in the complex. The observation of these therefore gives direct information as to whether a specific structure is possible or not. For arguments of this kind to be valid one must perform the activity analysis of the free components and the complex in their respective symmetry groups (10). It should be pointed out that these arguments are strongest in a negative proof, that is to say the observation of a transition can prove that certain structures are excluded but the lack of a transition can only be used as proof for a structure after discussions of expected intensities. Transitions that are allowed in the free components may be shifted in the complex. In favourable cases this may give direct information about the involvement of a certain atom or group in the bonding to the other part of the complex. Changes of relative intensities of vibrations may give rough estimates of changes in charge distribution on complex formation. Completely new vibrations involving the relative motions of the components appear (usually in the far-infrared region).

Information about isotope shifts of all vibrations of the same symmetry species as one of the rotations (of the complex), can be used to obtain quotients between moments of inertia which contain structural information, through the product rule (11). Sometimes structural parameters of one or both components may be approximately calculated although not all isotope shifts are available.

For weak complexes in particular the matrix isolation technique offers two important advantages over room temperature studies. At low temperature the equilibrium constants increase and make it possible to obtain higher concentrations of complex. The 10^{-1} very small band widths in matrix (often in the order of 1 cm^{-1}) make it much easier to distinguish between absorptions from the complex and the free components.

THE MATRIX ISOLATION TECHNIQUE

A matrix experiment involves the spectroscopic investigation of a solid solution formed by rapid cooling of a mixture of the substance under study and some diluent gas to a sufficiently low temperature to prevent diffusion and reaction. This is done by first mixing the substance with an appropriate amount of inert gas (usually nitrogen or rare gas) in a conventional vacuum system. The mixture is then allowed to flow through a metering valve and some kind of nozzle into a cryostat. In the cryostat the gas mixture is condensed on an optical window which is kept at low temperature (4-40 K depending on the matrix gas). When a sufficient amount of the mixture has been condensed on to the window, spectra are recorded and reactions may be initiated by photolysis or controlled diffusion may be performed by raising the temperature.

It is, however, important to realize that in practice this gives rise to a number of technical problems. Firstly, a cryostat is required for liquid helium or hydrogen equipped with an appropriate number of optical windows for the spectral regions of interest that, for various reasons (see further below), has to be capable of very long working cycles up to 5-10 days. Secondly, a very tight vacuum system, metering valve, nozzle and connections from the vacuum system to the cryostat are needed in order to minimize impurities. Thirdly, the process of condensation of the gas mixture on the cold window (usually called deposition) has to be done very slowly because the thermal conductivity of the solid is very low and too rapid deposition would heat the surface layer and allow long range diffusion

to take place. This has the consequence that deposition times as long as 20-50 hours often have to be used in order to acquire a sufficiently "thick", commonly 0.01-0.5 mm, matrix to allow good spectra to be recorded. Fourthly, matrix spectra are usually characterized by sharp absorptions and therefore spectra have to be recorded with rather high spectral resolutions. This can be very time consuming. A complete set of spectra may easily require 20-30 hours of recording time and often two or three sets of spectra are recorded, for instance before and after photolysis or diffusion. Fifthly, in order to avoid unwanted refraction of the spectrometer beam, which causes misfocusing, the nozzle has to give a uniform distribution of material over the cold window. Finally, in order to get matrices with as little scattering as possible, in order not to lose too much energy in the spectrometer, the best combination of deposition rate and deposition temperature for the specific matrix material has to be known and maintained constant throughout the deposition.

These purely technical problems can however be mastered and to a large extent have been for some time (12,13,14). The matrix isolation technique is now routinely used to study a great variety of problems, including hydrogen bonding, free radicals and high temperature species (15,16,17).

At this point it seems appropriate to discuss some general features of the infrared spectra obtained from matrix experiments. As stated earlier the absorptions are usually sharp and therefore the resolution of close lying transitions seldom represents any problem. The frequency shifts from gas phase to matrix are generally small; for benzene for instance no gas to matrix shift is larger than 17 cm^{-1} (N_2 matrix), and therefore assignments can often be made by direct comparison. Because of the rigidity of the matrix only very small molecules can rotate and therefore matrix spectra rarely show rotational fine structure (18,19). As a result moments of inertia cannot be obtained directly and the structural information contained in these has to be obtained by the above mentioned route via the product rule (11). As the temperature of the matrix is low, so called hot bands occur only if the molecule has very low frequency vibrations. At 20 K the frequency has to be less than 30 cm^{-1} to allow more than 10 % of the molecules to be in the excited state.

INSTRUMENTATION

The equipment used in this work is described in papers I and II. In the construction of the cryostat special interest was devoted to reliability and ease of operation. The cryostat has completed over 10000 duty hours and about as many stand-by hours with only two minor failures (one leak in the liquid nitrogen tank and one short-circuit in an electrical heater). The very accurate and simple to handle temperature control system, the long stand-alone times possible and the reliable system of warning and alarm signals have made continuous operation over long periods of time a routine procedure. Both the good temperature control and the possibility to record both UV- and IR-spectra on the same sample make the system very well fitted for complex studies. The constant flow double nozzle makes possible very reproducible depositions so that experiments with different concentrations can be compared with a minimum of corrections. It also allows studies of very reactive systems by separating the components of the complex completely until after the nozzles where they constitute two molecular beams directed at the cold window.

The temperature control of the cold window, the very constant deposition rate and the even distribution obtained by the nozzles all contribute to make the production of matrices of best possible optical quality a routine operation.

All UV- and VIS-spectra have been recorded on a Cary 15M instrument with ability to work at absorbances up till ca. 6. This is of considerable value with the often very intense absorptions of charge transfer spectra. Both the Perkin Elmer 521 (used in paper III) and the Perkin Elmer 180 (used in papers IV, V and VI) are infrared instruments of high quality. The more modern 180 is capable of higher resolution and is superior from a photometric point of view.

ADOPTION OF THE MATRIX ISOLATION TECHNIQUE TO COMPLEX STUDIES

In order to evaluate the possibilities and advantages as well as to find the difficulties and limitations of the matrix isolation technique for complex studies, a number of preliminary experiments (in total ca. 40) were done (paper III). These showed that in most cases the problems could be handled provided that experimental variables like deposition rate, deposition temperature, concentrations and diffusion temperatures were chosen with care.

During the continued work with the ethylene-chlorine complex (paper IV) it was found that when photochemically sensitive complexes are studied, a very efficient way of determining which absorptions that belong to the complex is to destroy the complex by photolysis and find out which absorptions decrease at the same rate. Some difficulties were encountered in preparing matrices with ethylene and chlorine without getting reaction already in the gas mixture. This was solved by making two separate gas mixtures, one of the nitrogen and chlorine and one of nitrogen and ethylene, and keeping them apart until just before they entered the nozzle, and by wrapping the vacuum system and connections with aluminium foil.

With the even more reactive systems like benzene-bromine, benzene-iodine chloride and in particular ammonia-chlorine (20) this procedure was insufficient. The problem was solved by the construction of the double nozzle mentioned earlier (paper II).

EXPERIMENTAL RESULTS

The results of papers III, IV, V and VI are most conveniently discussed by grouping the complexes with respect to donors. Three donors have been studied, water, ethylene and benzene, in all cases with a set of acceptors, mainly halogens, and on different levels of sophistication.

Water complexes. Complexes with nitric oxide, iodine (paper III) and chlorine (paper V) were studied. For the nitric oxide-water complex no detailed assignment was possible because of the formation of several complexes. In both the iodine and the chlorine complexes the very small shifts in the OH stretching frequencies, ca. 8 and 5 cm^{-1} , exclude the possibility of a hydrogen bonded structure, as the expected shifts on hydrogen bond formation are in the order of 100-1000 cm^{-1} . For both systems, signs of a second complex involving two water molecules were found but in neither case was the amount of data sufficient to allow any statements about the structure. For the studies of the water-chlorine complex, isotopically substituted water was used. The HOH angle was calculated from isotope shifts of the ν_3 vibration both for monomeric water and for the 1:1 complex. The angle was found to increase 0.4 degrees (if the numerically bad ^{16}O - ^{18}O pairs were excluded). This is probably barely significant considering that the formula used is only approximate for the complex. The CNDO calculations

favour a Y-shaped planar complex with an almost unchanged HOH angle (0.1 degree decrease) but the experimental data do not exclude a non-planar structure like that found for dioxan-halogen complexes (9).

Ethylene complexes. Complexes with sulphur dioxide, iodine (paper III) and chlorine were studied. The sulphur dioxide and iodine complexes were not studied in detail. For the chlorine complex use was made of H₄ and D₄ ethylene and the natural mixture of chlorine isotopes to calculate part of a force field for the complex in order to make comparisons with the force field calculated from CNDO calculations. Both experimental data and CNDO calculations support a C_{2v} symmetric complex, axial for CNDO, but it was not possible to choose between the axial and the resting structures from experimental data. Photolysis of the complex leads quantitatively to formation of 1,2-dichloroethane.

Benzene complexes. Complexes with chlorine, bromine and iodine chloride were studied (paper VI). The most extensive study was made of the bromine complex. The spectra of all complexes were found to be very similar, making it very reasonable to suppose that they have the same overall structure. The concentration dependency studies were made to make certain which absorptions should be assigned to the 1:1 complex and which should be assigned to higher complexes. By experiments with pure benzene it was established which absorptions that belonged to polymeric benzene. It was found that most of the symmetry forbidden transitions in monomer benzene became active in the complex and this was taken as evidence against the so called axial structure (21). For an axial structure only two of the forbidden fundamentals of benzene are expected to become active in the complex. From symmetry arguments alone no choice could be made between the two other proposed structures (21), the so called resting and oblique. But the stretching region of iodine chloride indicates that two isomeric forms of the 1:1 complex are present and this is clearly not possible for a resting structure. Therefore the results give strong support for the oblique structure.

Benzene halogen complexes have been studied several times before both in solution at room temperature (22) and in crystals (23,24). The conclusion made in this work is contrary to what has been stated earlier, but when one considers the often small shifts and intensities of the absorptions detected in this work it is by no means surprising if they have been overlooked earlier. It should also be noted, as has been pointed out

repeatedly by Mulliken (3), that this is one of the cases where extreme care has to be taken in trying to transfer the structure of $n:n$ complexes in crystals to isolated $1:1$ complexes.

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STUDENTLITTERATUR
LUND SWEDEN